Slow dynamics of glassy systems

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Abstract

In these lectures I will present an introduction to the modern way of studying the properties of glassy systems. I will start from soluble models of increasing complications, the Random Energy Model, the p-spins interacting model and I will show how these models can be solved due their mean field properties. Finally, in the last section, I will discuss the difficulties in the generalization of these findings to short range models.

1   Introduction

In these lectures I will study some systems which present some of the characteristics of glasses. The aim is to construct simple microscopic models which can be studied in details and still behave in interesting way. We will start from the simplest ones, where only some of the observed characteristics are reproduced and we will later go to more complex systems.

As usual we must select which of the many characteristics of glasses we think are important and should be understood. The main experimental findings about glasses that we would like to explain are the following:

- If we cool the system below some temperature (T_G), its energy depends on the cooling rate in a significant way. We can visualize T_G as the temperature at which the relaxation times become of the order of a hour.

- No thermodynamic anomaly is observed: the entropy (extrapolated at ultraslow cooling) is a linear function of the temperature in the region where such an extrapolation is possible. For finite value of the cooling rate the specific heat is nearly discontinuous. Data are consistent with the possibility that the true equilibrium value of the specific heat is also discontinuous at a temperature T_c lower than T_G.

- The relaxation time (and quantities related to it, e.g. the viscosity) diverges at low temperature. In many glasses (the fragile ones) the experimental data can be fitted as

$$\tau = \tau_0 \exp(\beta B(T)) \tag{1}$$
$$B(T) \propto (T - T_c)^{-\lambda} \tag{2}$$

1

where $\tau_0 \approx 10^{-13}s$ is a typical microscopic time, T_c is near to the value at which we could guess the presence of a discontinuity in the specific heat and the exponent λ is of order 1. The so called Vogel-Fulcher law [1] states that $\lambda = 1$. The precise value of λ is not well determine. The value 1 is well consistent with the experimental data, but different values are not excluded.

These lectures are organized as follows.

In section II we will study the Random Energy Model (REM) [2] ; the REM may seem to be a too simple model, however many of the main features of the model are present in more sophisticated versions, if the appropriate modifications are done.

In section III we will study some generalization of the REM in which the energies are not fully random, but are partly correlated. We will see that the isolated configurations which dominates the partition function of the REM are now promoted to valleys in a corrugated landscape.

Up to this moment we have been in the framework of the mean field theory in which all spins interacts among themselves. In section IV I will discuss how these results can be hopefully extended to models with short range forces, which are the new features and which a the points which are still to be solved.

2 The Random Energy Model

2.1 The definition of the model

The Random Energy Model [2] is the simplest model for glassy systems. It have various advantages: it is rather simple (its properties may be well understood with intuitive arguments, which may become fully rigorous) and display very interesting and new phenomena.

The Random Energy Model is defined as following. There are N Ising spins (σ_i, $i = 1, N$) which may take values ± 1; the total number of configurations is equal to $M \equiv 2^N$ and they can be identified by a label k in the interval $1 - M$.

Generally speaking the Hamiltonian of the system is given when we know the values of the energies E_k for each of the M configurations of the system. Usually one writes explicit expression for the energies as function of the configuration; on the contrary here we assume that the values of the E_k are random, with a probability distribution $p(E)$ which is Gaussian:

$$p(E) \propto \exp(-\frac{E^2}{2N}). \tag{3}$$

The partition function is simply given by

$$Z_{\mathcal{E}} = \sum_{k=1,M} \exp(-\beta E_k) = \int \rho(E) \exp(-\beta E), \tag{4}$$

$$\rho(E) \equiv \sum_{k=1,M} \delta(E - E_k). \tag{5}$$

The value of the partition function and of the free energy density ($f_{\mathcal{E}} = -\ln(Z_{\mathcal{E}})/(N\beta)$) depends on $\mathcal{E}$, i.e. all the values of the energies E_k. We would like to prove that when $N \to \infty$ the dependance on $\mathcal{E}$ of $f_{\mathcal{E}}$ disappears with probability 1. If this happens, the most likely value of $f_{\mathcal{E}}$ coincides with the average of $f_{\mathcal{E}}$, where the average is done respect to all the possible values of the energy extracted with the probability distribution eq. (3) .

The model is enough simple to be studied in great details; exact expressions can be derived also for finite N. Here we sketch the results giving a plausibility argument.

2.2 Equilibrium properties of the model

The crucial observation is the following. The probability of finding a configuration of energy E is

$$\mathcal{N}_0(E) \equiv 2^N \exp(-\frac{E^2}{2N}) = \exp(N(\ln(2) - \frac{1}{2}e^2)), \tag{6}$$

where $e \equiv E/N$ is the energy density. It is reasonable to assume (and it is confirmed by a detailed computation) that in the case of a generic system (with probability 1 when $N \to \infty$) no configurations are present in the region where $\mathcal{N}_0(E) << 1$, i.e. for

$$e^2 < e_c^2 \equiv 2\ln(2). \tag{7}$$

We can thus write for the generic choice of the energies $(\mathcal{E})$:

$$\rho(E) \approx \mathcal{N}(E) \equiv N_0(E)\theta(E_c^2 - E^2). \tag{8}$$

The partition function can be written as

$$\int \mathcal{N}(E) \exp(-\beta E). \tag{9}$$

Evaluating the integral with the saddle point method one finds that in the high temperature region, i.e.

$$\beta < \beta_c \equiv e_c^{-1}, \tag{10}$$

the internal energy density is simple given by $-\beta$. This behaviour must end somewhere because we know that the energy is bounded form below also when $\beta \to \infty$. Indeed in the low temperature region one finds that the integral is dominated by the boundary region $E \approx E_c$ and the energy density is exactly given by $-e_c$.

The entropy density is positive in the high temperature region, vanishes at β_c and remains zero in the low temperature region. It follows that in the high temperature region an exponentially large number of configurations contributes to the partition function, while in the low temperature region it is possible that the probability is concentrated on a finite number of configurations.

2.3 Properties of the low temperature phase

It is worthwhile to study in more details the structure of the configurations which mostly contribute to the partition function in the lower temperature phase. At this end it is useful to sort the configurations with ascending energy. We rename the configurations and we introduce new labels such that $(E_k < E_i$ for $k < i)$.

It is convenient to introduce the following quantity:

$$w_k \equiv \frac{\exp(-\beta E_k)}{Z}. \tag{11}$$

We have obviously that

$$\sum_{k=1,2^N} w_k = 1 \tag{12}$$

3

A detailed computation shows [2, 3, 4] that in the low temperature region (i.e. $\beta > \beta_c$) the previous sum is dominated by the first terms. Indeed

$$\sum_{k=1,L} w_k = 1 - O(L^{-\lambda}), \quad \lambda = \frac{1-m}{m}, \tag{13}$$

where

$$m = \frac{T}{T_c}. \tag{14}$$

In the same region the sum in the following equation is convergent and its average value is given by

$$\sum_{k=1,2^N} w_k^2 = 1 - m. \tag{15}$$

Generally speaking one finds that one can introduce the quantities F_k such that

$$w_k \propto \exp(-\beta F_k) \tag{16}$$

Here the variables F_k coincide with the total energy (not the energy density!) apart form an addictive constant. Their probability distribution at the lower end (which is the relevant region for thermodynamics in the low temperature region) can be approximated as

$$P(F) \approx \exp(\beta m F). \tag{17}$$

In this model everything is clear: in the high temperature region the number of relevant configurations is infinite (as usual) and there is a transition to a low temperature region where only few configuration dominates.

This phenomenon can be seen also in the following way. We introduce a distance among two configurations α and γ as

$$d^2(\alpha, \gamma) \equiv \frac{\sum_{i=1,N} (\sigma_i^\alpha - \sigma_i^\gamma)^2}{2n}. \tag{18}$$

Sometimes it is convenient to introduce also the overlap q defined as

$$q(\alpha, \gamma) \equiv \frac{\sum_{i=1,N} \sigma_i^\alpha \sigma_i^\gamma}{2N} = 1 - d^2(\alpha, \gamma). \tag{19}$$

The distance squared is normalized in such a way that it spans the interval $0 - 2$. It is equal to

- 0, if the two configuration are equal ($q = 1$).

- 1, if the configuration are orthogonal ($q = 0$).

- 2, if $\sigma_i^\alpha = -\sigma_i^\gamma$ ($q = -1$).

It is convenient to introduce the function $Q(d)$ and $P(q)$, i.e. the probability that two equilibrium configurations are at distance d or overlap q respectively. We find

- For $T > T_c$

$$Q(d) = \delta(d - 1), \quad P(d) = \delta(q). \tag{20}$$

- For $T < T_c$

$$Q(d) = (1 - A)\delta(d - 1) + A\delta(d), \quad P(d) = (1 - A)\delta(d) + A\delta(q - 1). \qquad (21)$$

where A is equal to $\sum_{k=1,2^N} w_k^2$. The average of A over the different realizations of system is equal to $1 - m$.

As soon as we enter in the low temperature region, the probability of finding two equal configurations is not zero. The transition is quite strange from the thermodynamic point of view.

- It looks like a *second* order transition because there is no latent heat. It is characterized by a jump in the specific heat (which decreases going toward low temperatures).

- It looks like a *first* order transition. There are no divergent susceptibilities coming form above of below (which beyond mean field theory should imply no divergent correlation length). Moreover the minimum value of d jumps discontinuously (from 1 to 0).

- If we consider a system composed by two replicas (σ^1 and σ^2) [5] and we write the Hamiltonian

$$H(\sigma^1, \sigma^2) = H(\sigma^1) + H(\sigma^2) + N\epsilon d^2(\sigma_1, \sigma^2) \qquad (22)$$

the thermodynamics is equal to that of the previous model (apart a factor 2) for $\epsilon = 0$, but we find a real first order thermodynamic transition, with a discontinuity in the internal energy, as soon as $\epsilon > 0$. The case $\epsilon = 0$ is thus the limiting case of real first order transitions.

These strange characteristics can be summarized by saying that the transition is of order one and half, because it share some characteristics with both the first order and the second order transitions.

It impressive to note that the thermodynamic behaviour of real glasses near T_c is very similar to the order one and half transition of REM. We will sea later that this behaviour is typical of the mean field approximation to glassy systems.

2.4 Dynamical properties of the model

The dynamical properties of the model can be easily investigated in a qualitative way (for more rigorous results sea [6]). Interesting behavior is present in the region where the value of N is large with respect to the time. Different results will be obtained for different definition of the dynamics if we consider some rather artificial form of the dynamics.

Let us first consider a single spin flip dynamics. In other words we assume that in a microscopic time scale scale, which for simplicity we consider of order unit, the system explore all the configurations which differ from the original one by a single spin flip and goes to one of them (or remain in the original one) with probability which is proportional to $\exp(-\beta H)$. This behaviour is typical of many dynamical process, like Glauber dynamics, monte Carlo, heath bath.

In this dynamical process each configuration C has N nearby configurations C' to explore. The energies of the configurations C' are uncorrelated to the energy of C, so that they would be of order one in most of the case. The lowest energy of the configurations

C' would be of order $-(N \ln(N))^{1/2}$, the corresponding energy density $(-(\ln(N)/N)^{1/2})$ vanishes in the large N limit.

If the configuration C has an energy density e less that zero, but greater than the equilibrium energy, the time needed to do a transition to a configuration of lower energy will be, with probability one, exponentially large.

For short times a configuration of energy e will be completely frozen. Only at larger times it may jump to a typical configuration of energy zero. At later times different scenarios are possible: the configuration comes back to the original configuration of of energy e or, after some wandering int the region of configurations of energy density ≈ 0, it fells in an other deep configuration of energy e'. A computation of the probabilities for these different possibilities has not yet been done, although it should not too difficult.

The conclusions of this analysis are quite simple.

- If we start from a random configuration, after a time which is finite when $N \to \infty$, the system goes to a configuration whose energy is of order $-\ln(N)^{1/2}$ and stops there.

- If we start from a random configuration and we study the system at exponentially large times the system will reach an energy density which may be different from the orginal one.

Similar results may be obtained if we consider a rather artificial dynamics in which we assume that in a microscopic time the system explore a number of configurations V which is order $\exp(Nh)$. The previous argument will tell us that the number of configurations, for which a transition is possible in times of order unit, is given by

$$\exp(N(h + s(e) - s(0))).\qquad(23)$$

where $s(e) = e^2/2$ is the entropy density as function of the energy density. The energy density which can be reached is therefore given by

$$\frac{e^2}{2} = h.\qquad(24)$$

Also this case the system freezes at non zero energy. The single spin flip limit correspond to $h = \ln(N)/N$.

3 Models with partially correlated energy

3.1 The definition of the models

The random energy model (REM) is rather unrealistic in that it predicts that the energy is completely upset by a single spin flip. This feature can be eliminated by considering a more refined model, the so called p-spins models [7, 8] , in which the energies of nearby configurations are also nearby. We could say that energy density (as function of the con-figurations) is not a continuous function in the REM, while it is continuous in the p-spins models, in the topology induced by the distance (eq. (18)). In this new case some of the essential properties of the REM are valid, but new features are present.

The Hamiltonian we consider depends on some control variables J, which have a Gaussian distribution and play the same role of the random energies of the REM and by the spin variable σ. For $p = 1, 2, 3$ the Hamiltonian is respectively

$$H_J^1(\sigma) = \sum_{i=1,N} J_i \sigma_i \tag{25}$$

$$H_J^2(\sigma) = \sum_{i,k=1,N}' J_{i,k} \sigma_i \sigma_k \tag{26}$$

$$H_J^3(\sigma) = \sum_{i,k,l=1,N}' J_{i,k,l} \sigma_i \sigma_k \sigma_l$$

where the primed sum indicates that all the indices are different. The variables J must have a variance of $O(N^{(1-p)/2})$ in order to have a non trivial thermodynamical limit.

It is possible to prove by am explicit computation that if we send first $N \to \infty$ and later $p \to \infty$, one recover the REM. Indeed the energy differences corresponding to one spin flip are of order p for large p (they ar order N in the REM, so that in the limit $p \to \infty$ the energies in nearby configurations become uncorrelated and the REM is recovered.

3.2   Equilibrium properties of the models

The main new property of the model is the correlation of energies. This fact implies that if C is a typical equilibrium configuration, all the configurations which differ from it by a finite number of spin flips will also have a finite energy. The equilibrium configurations are no more isolated (as in REM), but they belongs to valleys, such that the entropy restricted to a single valley is proportional to N and it is and extensive quantity.

The thermodynamical properties at equilibrium can be computed using the replica method [3, 4] . In the simplest version of this method [7, 8] one introduces the typical overlap of two configurations inside the same valley (sometimes denoted by q_{EA}. Something must be said about the distribution of the valleys. Only those which have minimum free energy are relevant for the thermodynamics. One finds that these valleys have zero overlap and have the same distribution of free energy as in the REM

$$P(F) \propto \exp(\beta m (F - F_0)). \tag{27}$$

Indeed the average value of the free energy can be written in a self consistent way as function of m and q ($f(q, m)$) and the value of these two parameters can be found as the solution of the stationarity equations:

$$\frac{\partial f}{\partial m} = \frac{\partial f}{\partial q} = 0. \tag{28}$$

The quantity q (which would be 1 in the REM) is here of order $1 - \exp(-A\beta p)$ for large p, while the parameter m has the same dependence of the temperature as in the REM, i.e. 1 at the critical temperature, and a linear behaviour al low temperature. The only difference is that m is no more strictly linear as function of the temperature.

The thermodynamical properties of the model are the same as is the REM: a discontinuity in the specific heat, with no divergent susceptibilities.

3.3 The Free energy landscape

It would be interesting to characterize better the free energy landscape of the model, especially in order to understand the dynamics. Indeed we have already seen that in the REM the system could be trapped in metastable configurations. Here the situation is more complicated. Although the word *valley* has a strong intuitive appeal, we must first define what a valley is in a more precise way.

There are two different (hopefully equivalent) definitions of a valley:

- A valley is a region of configuration space separated by the rest of the configuration space by free energy barriers which diverge when $N \to \infty$. More precisely the system, in order to go outside a valley by moving one spin at once, must cross a region where the free energy is higher that of the valley by a factor which goes to infinity with N.

- A valley is a region of configuration space in which the system remains for time which goes to infinity with N.

The rationale for assuming that the two definitions are equivalent is the following. We expect that for any reasonable dynamics in which the systems evolves in a continuous way (i.e. one spin flip at time), when it goes from a valley to an other valley, the system must cross a configuration of higher free energy and therefore the time for escape from a valley is given by

$$\tau \simeq \tau_0 \exp(\beta \Delta F) \tag{29}$$

where ΔF is the free energy barrier.

It is crucial to realize that in infinite range models there can be valley which have an energy density higher that that of equilibrium states. This phenomenon is definitely not present in short range models. No metastable states with infinite mean life do exist in nature.

Indeed let us suppose that the system may stay in phase (or valleys) which we denote as A and B. If the free energy density of B is higher than that of A, the system can go from B to A in a progressive way, by forming a bubble of radius R of phase A inside phase B. If the surface tension among phase A and B is finite, has happens in any short range model, for large R the volume term will dominate the free energy difference among the pure phase B and phase B with a bubble of A of radius R. This difference is thus negative at large R, it maximum will thus be finite. In the nutshell a finite amount of free energy in needed in order to form a seed of phase A starting from which the spontaneous formation of phase A will start. For example, if we take a mixture of H_2 and O_2 at room temperature, the probability of a spontaneous temperature fluctuation in a small region of the sample, which lead to later ignition and eventually to the explosion of the whole sample, is greater than zero (albeit quite a small number), and obviously it does not go to zero when the volume goes to infinity.

We have two possibilities open in positioning this mean field theory prediction of existence of real metastable states:

- We consider the presence of these metastable state with *infinite* mean life an artefact of the mean field approximation and we do not pay attention to them.

- We notice that in the real systems there are metastable states with very large (e.g. much greater than one year) mean life. We consider the *infinite* time metastable

states of the mean field approximation as precursors of these *finite* states. We hope (with reasons) that the corrections to the mean field approximation will give a finite (but large) mean life to these states (how this can happen will be discussed in the next section).

Here we suppose that the second possibility is the most interesting and we proceed with the study of the system in the mean field approximation. The strategy for investigate the properties of these metastable states consists in considering systems with R replicas (two or more) of the same system with Hamiltonian given by

$$\beta H = \sum_{r=1,R} \beta_r H(\sigma^r) + \sum_{r,s=1,R} \epsilon_{r,s} q_{r,s}. \tag{30}$$

Different replicas may stay at different temperature. The quantities ϵ are just Legendre multipliers needed to enforce specific value of the the overlaps q. In this way (let us consider for simplicity the case where all temperature are zero) we find (after a Legendre transform) a free energy density as function of the q.

Let us consider for simplicity the case where we set

$$q_{1,r} = q \quad \text{for} \quad r = 2, R \tag{31}$$

($q_{r,r}$ is identical equal to 1) and the others q are left free [5] . A simple computation show the final free energy density that we obtain (let us call $f_R(q)$ is given by

$$f_R(q) - Rf = - \lim_{N \to \infty} \frac{\ln \left(\sum_\sigma \left(\sum_\tau \delta(q(\sigma,\tau) - q) \right)^{(R-1)} \right)}{\beta N} \equiv \tag{32}$$

$$- \lim_{N \to \infty} \frac{\ln < P_\sigma(q)^{(R-1)} >}{\beta N}, \tag{33}$$

where f is the unconstrained free energy.

A particular case, which is very interesting, is given by the limit $R \to 1$ [9, 10] :

$$W(q) \equiv \lim_{N \to \infty} \frac{\ln(P_\sigma(q))}{\beta N} = \frac{\partial (f_R(q) - Rf)}{\partial R}|_{R=1} \tag{34}$$

The potential $W(q)$ has usually a minimum at $q = 0$, where $W(0) = 0$. It may have a secondary minimum at $q = q_D$. We can have three quite different situations

- $W(q_D) = 0$. This happens in the low temperature region, below T_c, where we can put two replicas both at overlap 0 and at overlap q_{EA} without paying any prize in free energy. In this case $q_D = q_{EA}$.

- $W(q_D) > 0$. This happens in an intermediate temperature region, above T_c, but below T_D, where we can put one replica σ at equilibrium and have the second replica τ in a valley near it. It happens that the internal energy of both the σ configuration (by construction) and of the τ configuration are equal to the equilibrium one. However the number of valley is exponentially large so that the free energy a single valley will be smaller. One finds in this way that $W(q_D) > 0$ is given by

$$W(q_D) = \frac{\ln \mathcal{N}_e}{N} \tag{35}$$

where $\mathcal{N}_e$ is the average number of the valleys having the equilibrium energy [11, 12] .

9

- At $T > T_D$ the potential $W(q)$ has only the minimum at $q = 0$. The quantity q_D cannot be defined and no valley with the equilibrium energy are present. This is more or less the definition of the dynamical transition temperature T_D. A more careful analysis shows that for $T_D < T < T_V$ there are still valleys with energy *less* than the equilibrium one, but these valleys cover a so small region of phase space that they are not relevant for equilibrium physics.

It is also possible to study the properties of the free energy for $R \neq 1$ we can force the σ configuration to be not an equilibrium one and in this way we controll the properties of the valleys having an energy different than the equilibrium one. This method can give rather detailed information on the free energy landscape, which I do not have time to discuss in details and which have not yet yet fully studied.

The most interesting result is that for $T < T_D$ the entropy of the system can be written as

$$S = S_V + W \tag{36}$$

where S_V is the entropy inside a valley and W is the configurational entropy, or complexity, i.e. the term due to the existence of an exponentially large number of states. The W contribution vanishes at T_c and becomes exactly equal to zero for $T < T_c$ [13, 14, 15] .

In the REM limit ($p \to \infty$) the temperature T_D goes to infinity. In this limit the third region does not exist. Therefore the dynamical transition is a new feature which is not present in the REM.

3.4 Mode coupling theory at short times

The simplest way to study the dynamics of the problem is to consider a system which evolves according to Langevin equation of to some sort of Glauber dynamics. For example we can suppose that:

$$\frac{d\sigma_i}{dt} = -\frac{\delta H}{\sigma_i} + \eta_i(t), \tag{37}$$

where η is an appropriate white noise.

In this model is convenient to introduce the single site correlation function (C) and the response (G) function of the times. One finds that they can be defined as

$$C(t_1, t_2) = < \sigma_i(t_1)\sigma_i(t_2) > \tag{38}$$

$$G(t_1, t_2) = < \frac{\delta\sigma_i(t_1)}{h_i(t_2)} > \tag{39}$$

where $h(t)$ is an external magnetic field.

If the systems is at equilibrium (or in a metastable state), the correlation and the response functions will depend only on the time difference. If the system is out of equilibrium these functions will depend in a non trivial way from both the arguments.

In both cases one can write down closed equations for the correlation functions in the case where the size N goes to infinity at fixed times [16] . These equations have a rather complex structure. We could discuss two different regimes:

1. We start at time zero from an equilibrium configuration.

2. We start at time zero from a random configuration.

In the first case we find that, if we approach the dynamical temperature from above, the correlation time diverges a a power of $T - T_D$, and the usual analysis of the mode coupling theory can be done in this region. Mode coupling theory is essentially correct in this region.

In the second case one finds that below the dynamical transition, the energy does not go anymore to the equilibrium value, but it goes to an higher value, which in some cases can be computed analytically.

The phenomelogy is rather complex, the aging properties of the systems are particularly interesting, but we cannot discuss them for lack of space. It is interesting to note that the mode coupling theory become exact in the mean field theory and describes what happens nearby the dynamical phase transition at T_D, which is a temperature higher that the equilibrium transition temperature at T_c.

3.5   Dynamical properties of the models from a landscape analysis

Here we would like to understand the dynamical properties of the model starting from results which we have already derived on the free energy landscape without having to compute explicitly the solution of the equation of motion for the correlations C and G. This can be done by assuming the this very slow dynamics is an activated process dominated by barrier crossing and that the height of the barriers can be computed using the method of the previous sections.

Some of the question we ask are the following:

- How long does a system remains in the same valley?

- If the system is out equilibrium at time 0, which is the asymptotic value of the energy at large times?

The results are similar to those obtained by the explicit dynamical analysis of the previous section. We obtain also more detailed information on the region where the time scale is exponentially large. This region can be studied only with very great difficulties using the dynamical equations.

In the first case (i.e.the system start from a thermalized configuration) below T_D, the system is confined to a valley. A first estimate of the time needed to escape from a valley can be obtained as follows. We introduce the parameter

$$q(t) \equiv \frac{\sum_{i=1,N} \sigma_i(0)\sigma_i(t)}{N}. \tag{40}$$

We assume that on the large time scale the evolution of q is more or less the same of a system with only one degree of freedom with potential $W(q)$. This assumption is not completely correct, but it is likely to be enough to give a first estimate (to be refined later) of the escape time. Therefore it is reasonable to assume that in a first approximation the the time needed to escape from the valley is given by

$$\tau = \tau_0 \exp(N\beta\Delta W), \tag{41}$$

where ΔW is the difference in free energy among the minimum at q_D and the maximum al lower values of q.

For large time (but not exponentially divergent with N) we have that

$$\lim_{t \to \infty} q(t) = q_D. \tag{42}$$

Eventually the system will escape from a valley for times greater that τ.

In the other situation (the system is originally out equilibrium) things are more complicated. Metastable valleys of high energies do exist, however it is not clear that a system cooled from an high temperature region must be trapped in the valley with high energy. Indeed it will be trapped in the valley with largest attraction domain, but the properties of the valley cannot be found if we do not use the dynamics in an explicit way. Some educated conjectures can be done, but the question has never been investigated in details. The problem is not easy, because the system is strongly out of equilibrium.

A better understanding comes if we consider the case in which the system is slowly cooled, from high to low temperature. We consider here that case of slow, not ultra slow, cooling, i.e. the time scale if fixed when N goes to infinity. In this case it is reasonable to assume that the system frozen in a valley at the dynamical temperature and we have to follow the energy of that valley when we cool. That can be done by using the formulation with different replicas at different temperatures. In this way one finds that the system is frozen in a configuration which is near to the configuration at the dynamical temperature.

A detailed comparison of the results for the energy of the metastable states obtained by doing different assumption is still lacking, but is should be not too difficult.

4 More realistic models

4.1 General consideration on long range Hamiltonians with and without quenched disorder

A peculiar phenomenon, that is present in Hamiltonians when the range is infinite, is the partial equivalence of Hamiltonians with quenched and random disorder. An example is the following.

The configuration space is given by N Ising spin variables. We consider the following Hamiltonian

$$\sum_{i=1,N} ||B_i|^2 - 1|^2, \tag{43}$$

$$B_i = \sum_{k=1,N} R_{i,k} \sigma_k. \tag{44}$$

where R is an unitary matrix, i.e.

$$\sum_{k=1,N} R_{i,k} \overline{R_{k,m}} = \delta_{i,m}. \tag{45}$$

We could consider two different cases [18] :

- The matrix R is a random orthogonal matrix.

- The matrix R is given by

$$R(k, m) = \frac{\exp(2\pi i \ km)}{N^{1/2}} \tag{46}$$

In other words B is the Fourier transform of σ.

The second case is a particular instance of the first one, exactly in the same way that a sequence of all zeros is a particular instance of a random sequence.

The first model can be studied using the replica method and one finds results very similar to those of the p-spin model we have already studied.

Now it can be proven that the statistical properties of the second model ar identical to those of the first model, with however an extra phase. In the second model (at least for some peculiar value of N, e.g. N prime, [17, 18, 19]) there are configurations which have exactly zero energy. These configuration form isolated valleys which are separated from the others, but have much smaller energy and they have a very regular structure (like a crystal). An example of these configurations is

$$\sigma_k \equiv {}_{\mathrm{mod}\ N}\ k^{(N-1)/2} \tag{47}$$

(The property $k^{(N-1)} \equiv 1$ for prime N, implies that in the previous equations $\sigma_k = \pm 1$). Although the sequence si_k given by the previous equation is apparent random, it satisfies so many identities that it must be considered as an extremely ordered sequence (like a crystal). One finds out that from the thermodynamical point of view it is convenient to the system to jump to one of these ordered configurations at low temperature. More precisely there is a first order transition (like a real crystalization transition) at a temperature, which is higher that the dynamical one.

If the crystallisation transition is avoided by one of the usual methods, explicit interdiction or sufficient slow cooling, the properties of the second model are exactly the same of those of the first model. Similar considerations are also valid for other spin models [20, 21, 22] or for model of interacting particles in very large dimensions, where the effective range of the force goes to infinity [24, 23, 25] .

We have seen that by removing the quenched disorder in the Hamiltonian had a quite positive effect: a crystallisation transition is also present like in some real systems. If we neglect crystalization, which is absent for some values of N, no new feature is present in system without quenched disorder. As we shall see later the equivalence of short range systems with and without quenched disorder is an interesting and quite open problem.

4.2   Short range models

We have already seen that in a short range model we cannot have real metastable states. Let us see in more details what happens.

Let us assume that $\Delta f < 0$ is the difference in free energy among the metastable state and the stable state. Now let us consider a bubble of radius R of stable state inside the metastable one. The free energy difference of such a bubble will be

$$F(R) = -\Delta f\ V(R) - I(R) \tag{48}$$

where the interfacial free energy $I(R)$ can increase at worse as $\sigma \Sigma(R)$. the quantities $V(R) \propto R^D$ and $\Sigma(R) \propto R^{D-1}$ are the volume and the surface of the bubble and σ is the surface tension, which can also be zero (when the surface tension is zero, we have $I(R) \propto R^\omega$, with $\omega < D - 1$).

The value of $F(R)$ increases at small R, reaches a maximum a R_c, which in the case $\sigma \neq 0$ is of order $(\Delta f)^{-1}$ and it becomes eventually negative at large R. According to enucleation theory, the system goes from the metastable to the stable phase under the

formation and the growth of such bubbles, and the time to form one of them is of order (neglecting prefactors)

$$\ln(\tau) \propto \Delta f \ R^D \propto (\Delta f)^{(D-1)} \tag{49}$$

$$\tau \propto \exp(\frac{A}{(\Delta f)^{(D-1)}}) \tag{50}$$

where A is constant dependent on the surface tension. In the case of zero surface tension we have

$$\tau \propto \exp(\frac{A}{\Delta f^\lambda}) \tag{51}$$

$$\lambda = \frac{D}{\omega} - 1 \tag{52}$$

This argument for the non existence of metastable states can be naively applied here. The metastable states of the the mean field approximation now do decay. The dynamical transition becomes a smooth region which separates different regimes; an higher temperature regime where mode coupling theory can be approximately used and a low temperature region where the dynamics is dominated by barriers crossing. There is no region where the mode coupling theory becomes exact but it is only an approximated theory which describe the behaviour in a limited region of relaxation times (large, but not too large).

The only place where the correlation time may diverge is at that the thermodynamical transition T_c, whose existence seems to be a robust prediction of the mean field theory. It follows that the only transition, both from the static and the dynamical point of view, is present at T_c.

In order to understand better what happens near T_c we must proceed in a careful matter. The nucleation phenomenon which is responsible of the decay of metastable states is of the same order of other non-perturbative corrections to the mean field behaviour, which cannot be seen in perturbation theory. We must therefore compute in a systematic way all possible sources of non perturbative corrections. This has not yet been done, but it should not be out of reach.

One of the first problem to investigate is the equivalence of systems with and without random disorder. In systems with quenched disorder there are local inhomogeneities which correspond to local fluctuations of the critical temperature and may dominate the thermodynamics when we approach the critical temperature [26] .

It is quite possible, that systems with and without quenched disorder, although they coincide in the mean field approximation, they will be quite different in finite dimension (e.g. 3) and have different critical exponents. The scope of the universality classes would be one of the first property to assess.

It is not clear at the present moment if the strange one order and half transition is still present in short range model or if it is promoted to a bona fide second order transition. If the transition remains of the order one and half (for example is conceivable that this happens only for systems without quenched disorder). It could also possible that there is appropriate version of the enucleation theory which is valid near T_c and predicts:

$$\tau \propto \exp(\frac{A}{(T - T_C)^\alpha}). \tag{53}$$

14

A first guess for α is $D - 2$ [15, 9] , although other values, e.g. 2/3, are possible. A more detailed understanding of the static properties near T_c is needed before we can do any reliable prediction.

It seems to me that the theoretical situation is quite good: we do not have yet the answers to our questions, but is seems that we are starting to ask the right questions. There is a lot of hard work waiting for us.

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